



Heterogeneous behaviour of the lithium battery composite electrode LiFePO_4

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HIGHLIGHTS

- Structural and electronic modifications of a battery electrode were observed *operando*.
- A heterogeneous behaviour of the electrode is clearly evidenced.
- The redox process is mapped at a micrometre scale.
- The heterogeneity is influenced by cycling regime, pressure, formulation.

ARTICLE INFO

Article history:

Received 20 July 2012

Received in revised form

23 October 2012

Accepted 16 November 2012

Available online 23 November 2012

Keywords:

Lithium battery

Synchrotron

Operando

Mapping

ABSTRACT

To improve the performance of the positive electrode in batteries, it is important to thoroughly characterize these materials during battery cycling, beyond just electrochemical characterization. Among the very few techniques available for *operando* studies, X-ray Absorption Spectroscopy (XAS) appears very powerful, with high spatial and time resolutions provided by synchrotron radiation. Moreover XAS is well known for its capabilities in charge transfer and structure determinations, both being the major changes induced by electrochemical cycling of electrode materials. By an appropriate combination of three XAS beamlines using a specially designed electrochemical cell, we have studied composite positive electrodes made with LiFePO_4 as the active material. We directly observed the heterogeneity of the electrode during operation, some parts being delayed and others advanced, compared to the mean charge state of the electrode. A mapping of this heterogeneity was made at different length scales.

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1. Introduction

In the global context of the increasing demand of energy storage capabilities, huge research and technological activity is devoted to the improvement of lithium batteries performance. Progress is achieved through a better understanding of the general functioning of the batteries and their different elements: electrodes, electrolyte, interfaces. For technical reasons, despite the evident interest in studying the batteries during their functioning, most of the techniques used for the battery characterization, except the electrical measurements themselves, have been performed at rest, after a partial or complete charge or discharge, or at a slow rate.

Recent studies have clearly demonstrated the major role played by the formulation and the processing of composite electrodes in battery performance [1]. The electrode formulation takes into

account the particle size, and the proportions of active material, conductive additive and polymer insuring porosity and mechanical performance. The main issue is the connectivity of the active material particles to the electron conducting network and to the electrolyte, that insures an efficient and fast transfer of the electrons and lithium ions respectively [2]. Ideally, these two charged species have to go in and out the particles in the same quantities at the same speed. If it is not the case, the transformation of the corresponding particle will probably be delayed, as compared to the mean charged state obtained by the electrochemical measurement of the complete electrode. In order to compensate for such a delay, well connected particles must be more transformed. Such behaviour will induce, at least before equilibrium, significant heterogeneities in the electrode. This issue has been addressed by some groups either in using spectroscopies at rest [3] or by thermodynamic considerations [4]. Therefore, an important still pending question is: “What is the degree of homogeneity, in lithium and electron content, of an electrode during its functioning?”

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Table 1

Surfaces of the electrodes, the beams and the particles used in this study. Data collection times and acquisition modes for the different beamlines.

Element	Electrode	SAMBA beam	ODE beam	LUCIA beam	Clusters of crystallites	Crystallites
Surface size (μm^2)	1.10^8	12×10^5	1250	49	300	18×10^{-3}
Time (mode)		10 mn (static) 1 s (quick)	0.1 s (dispersive)	3 s per point (static)		

In order to answer this question, synchrotron experiments gather all the requirements in the X-ray diffraction (XRD) and X-ray absorption spectroscopy (XAS) techniques that have proved their capabilities in atomic and electronic structure characterizations [5–9]. Due to the very high flux that synchrotron sources are able to deliver, and to the technical developments of new beamlines, XAS beamlines may combine the appropriate time and space resolutions.

Several groups have used XRD and XAS synchrotron techniques to characterize LiFePO_4 positive electrodes under electrochemical operation. XRD experiments have been performed by Chang et al. [10] and Shin et al. [11] in dynamic mode, but without paying a special attention to the spatial resolution. They put in evidence some “delay” in the phase transformation, and explained it by a partial amorphisation. In a recent study we have confirmed this apparent delay [12] but demonstrated that no amorphisation occurred in our electrodes. More recently, Liu et al. [13] have spatially studied *ex situ*, and therefore not in a dynamic mode, the phase transformation of LiFePO_4 into FePO_4 within electrodes after their functioning in batteries. Nevertheless, after a high rate charge, they observed a large heterogeneity of the oxidation process through the electrode from the current collector to the electrolyte side. A. Dheb et al. [14] and [15] have performed precise XAS experiments but only *in situ*, without any consideration of time or space resolution. To advance understanding of these processes, we have undertaken XAS experiments with various time and space resolutions.

2. Time and space resolutions

Homogeneity refers to a spatial resolution, expressed in absolute value (probe size) or in relative values: probe size/electrode size and probe size/particle or crystallite size. *Operando* study of a battery implies that the experiments are performed in a small fraction of time as compared to the duration of the electrochemical event, as a charge or discharge. It seems reasonable to consider that the data collection time must be lower than one percent of the

studied phenomenon, corresponding to about 30 s for a charge or discharge at a 1C rate.

We have performed XAS experiments at the iron K-edge in the Li_xFePO_4 ($0 \leq x \leq 1$) electrode material, with various time and space resolutions provided by three different beamlines on the third generation synchrotron source SOLEIL. These beamlines are SAMBA for Quick XAS experiments, ODE for dispersive XAS (high time and spatial resolutions) and LUCIA for high spatial resolution [16]. The experiments have been conducted on LiFePO_4 particles prepared according to Delacourt et al. [17] and [18]. Comparison of the sizes of these electrodes with that of the beams and of the crystallites (or primary particles) and their clusters (or secondary particles) is presented in Table 1, along with the data collection times.

3. XAS evidence of an apparent delay

A delay in the structural transformation of LiFePO_4 into FePO_4 has already been observed by XRD [10]. The occurrence of an amorphous phase has been claimed as an explanation for this delay [19]. However, our former results [12] on this topic, presenting the careful fit of reflection peak intensities of diffraction patterns collected *operando*, tend to prove that no amorphous phase was created, since all the disappearing LiFePO_4 phase was accompanied by the equivalent formation of FePO_4 during the charge process. Some XAS preliminary experiments [12] have confirmed the delay. Because XAS is not sensitive to the crystalline state of the studied material, the formation of such a third amorphous phase, in a significant amount, cannot simply explain the delay. A complete charge in 1 h (1C rate) in the Quick XAS mode (1 s per spectrum) allowed observation of the continuous evolution of the XAS spectra (Fig. 1a). First of all, the presence of well defined isosbestic points is a clear signature of the biphasic nature of the system [20] and [21]. As a consequence, the spectra for all compositions between LiFePO_4 (red) and FePO_4 (blue) are Linear Combination Fit (LCF) of these end – composition spectra. The proportions of the two phases extracted from these LCF's confirm the apparent delay (Fig. 1b).

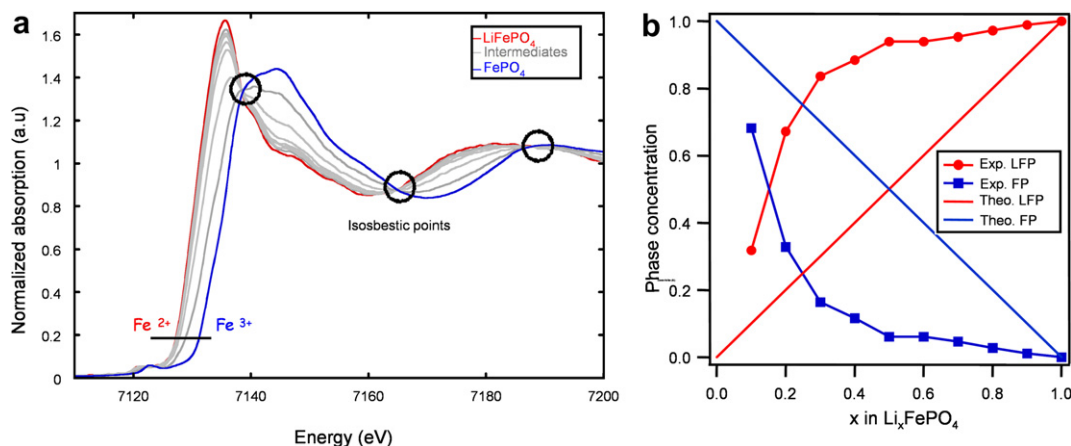


Fig. 1. (a) Normalized XANES spectra at the Fe K-edge during charge at 1C rate. LiFePO_4 (red) and FePO_4 (blue) spectra taken at equilibrium are plotted for comparison. (b) Evolution of LiFePO_4 (red) and FePO_4 (blue) percentages, deduced from Linear Combination Fits, plotted as function of x Li amount. The straight lines correspond to normal evolutions of both proportions for any part of a homogeneous electrode.

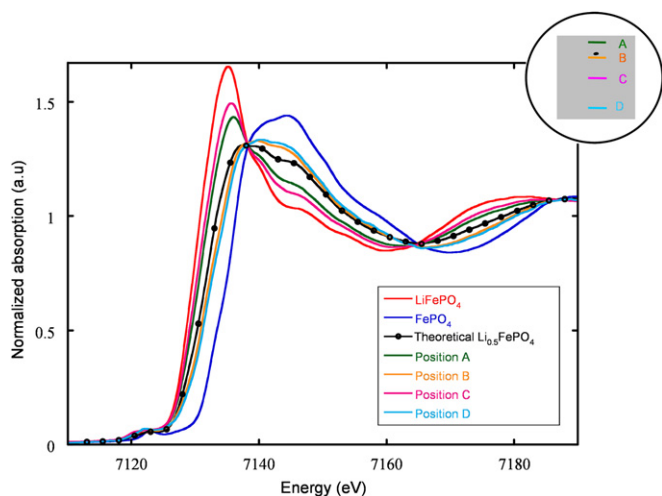


Fig. 2. X-ray absorption spectra of LiFePO_4 (red), FePO_4 (purple), linear combination corresponding to the theoretical $\text{Li}_{0.5}\text{FePO}_4$ composition (black circle) and spectra collected at different beam positions (A–D) on the electrode. Insert shows these positions on the square electrode. Dotted circle represents the position of the hole into the cell [12].

4. XAS evidence of heterogeneity

By combining XRD and XAS techniques we have confirmed the two-phase reaction character of the delithiation of LiFePO_4 and excluded any amorphous phase formation. Therefore, we hypothesized that the existence of some parts of the electrode with a composition lower than the global lithium content of the

electrode (electrochemical determination) would induce higher compositions for other parts. In order to probe such heterogeneity of the electrode, we have withdrawn the electrode from the experimental cell after reaching the global electrochemical composition $\text{Li}_{0.5}\text{FePO}_4$ through a charge at 1C rate. Fig. 2 shows the XANES spectra collected on the SAMBA beamline for this composition on four different positions of the electrode.

It is obvious, and of much interest, that the four different positions give different spectra. They are also different from the theoretical spectrum, in black, obtained from the 50/50 linear combination between the end spectra, in red and purple. Two of them, A and C, are “delayed” and two others, B and D, are slightly “in advance”.

These spectra have been collected on an electrode kept at rest and we found important to examine the behaviour of such LiFePO_4 electrodes during cycling. For this purpose, measurements have been performed on the ODE beamline, with a spectrum obtained every 0.1 s with a beam size lower by three orders of magnitude (Table 1). A displacement of the electrode during the measurements allowed probing simultaneously both possible delay/advance and the correlated heterogeneity. Seven different points were considered and Fig. 3a and b present the evolution of the spectra for two of them. The raw data clearly show the different behaviour of these two points and confirm the heterogeneity of the electrode. From the data, the LCFs allow quantification of the proportions of the two end phases and evaluation of the delay or advance (Fig. 3c). We may notice that point 1 is less delayed than point 5, and is slightly delayed only after extraction of 0.4 Li (composition $\text{Li}_{0.6}\text{FePO}_4$). It is important to notice that, even if some of them may be largely delayed, all the observed points reach the global electrochemical composition at the end of charge. This proves that, at this scale, all these points are connected to the

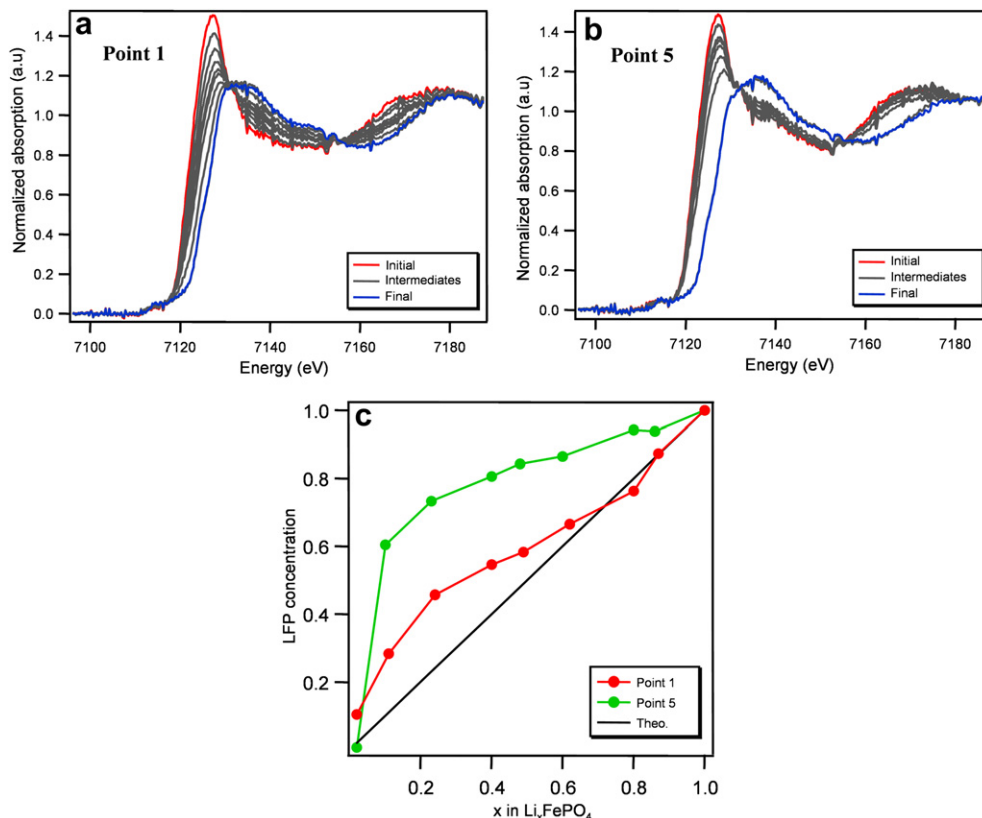


Fig. 3. (a) and (b) Normalized XANES spectra for different Li_xFePO_4 compositions recorded on two different points of the electrode. (c) Evolution of LiFePO_4 percentage on these points during the charge at 1C rate.

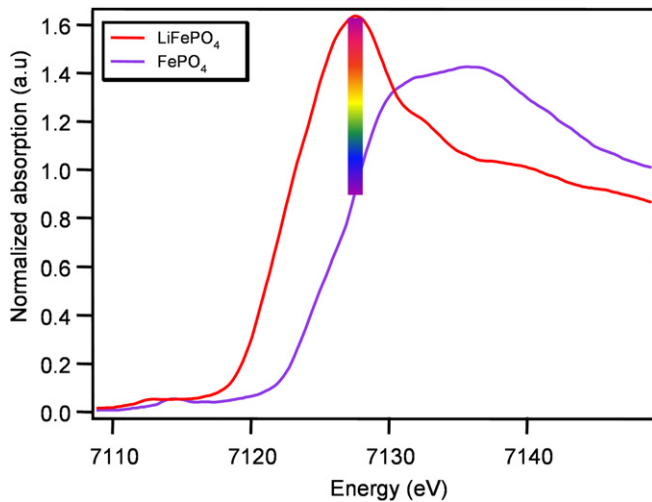


Fig. 4. X-ray absorption spectra of LiFePO_4 (red), FePO_4 (purple). Maximum of absorption difference between these two phases is indicated, and colour code attributed for the mean iron oxidation state (see Fig. 5).

electron and ion collectors, even if each is connected in a more or less efficient way.

5. Mapping of the electrode

As we proved by XAS that the apparent “delay” is a consequence of Li^+ or electron diffusion heterogeneity, it is important to study it by mapping. We have undertaken mapping experiments at the LUCIA beamline, especially designed for such experiments with

a monitored displacement of the sample. This beamline is equipped with a classical step by step monochromator that is not appropriate for fast data collection. As a matter of fact, one complete XANES spectrum, as those shown on Fig. 4, would have been collected in about 5 min. Therefore it is clear that such a process is not appropriate for any dynamic study. Moreover, a significant mapping of about 1300 points for a battery at rest for only one composition would take at least 4 days, a duration incompatible with the use of any synchrotron source.

Therefore, we have used the large difference between the spectra of LiFePO_4 and FePO_4 (Fig. 4) to perform experiments at a fixed energy and to map the electrodes either during the functioning (3 s per point) or at different equilibrium states. This was especially possible because the two-phase nature of the process implies that, at any energy, the recorded absorption intensity is the linear combination of the intensities of the end phases and allows a direct measurement of the $\text{Fe}^{\text{II}}/\text{Fe}^{\text{III}}$ ratio. Due to the fact that the absorption is also correlated to the iron density in each point, it was necessary to map this density before starting the battery cycling and to normalize the subsequent data by these initial values.

We followed the variation of the X-ray absorption at the energy of 7127.2 eV. This value corresponds to the maximum of the spectrum for LiFePO_4 and the largest difference between the two spectra (Fig. 4). The electrode has been mapped with a spatial resolution of $7 \times 7 \mu\text{m}^2$. The chosen colour is red for pure Fe^{II} (LiFePO_4) and purple for pure Fe^{III} (FePO_4).

Data have been collected simultaneously in transmission mode, through a hole designed in the cell [12], and in fluorescence mode. In transmission, only 12.5 mm^2 can be mapped but the mapping is representative of the total thickness of the electrode. In fluorescence, the entire surface of the positive electrode can be studied but at about $7 \mu\text{m}$ depth. Fig. 5 represents the maps obtained in the fluorescence mode for the global compositions $x = 1, 0.8, 0.5, 0.2$,

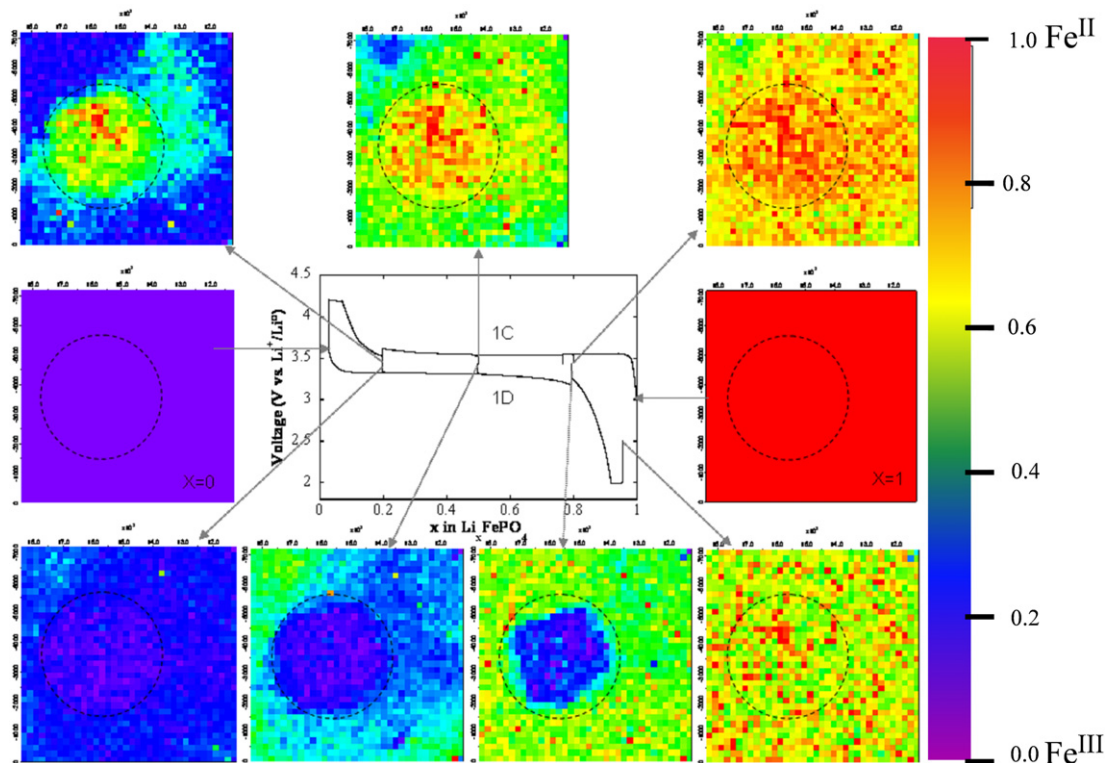


Fig. 5. Large area maps obtained in fluorescence mode during Open Circuit Voltage (OCV) at several Li_xFePO_4 compositions during charge and discharge at 1C rate. The square is $1 \text{ cm} \times 1 \text{ cm}$. Dotted circle shows the position of the plunger's hole (diameter 4 mm).

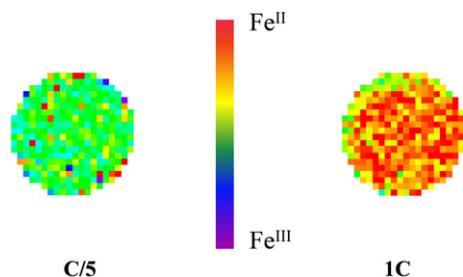


Fig. 6. Large area maps obtained in transmission mode during OCV at $\text{Li}_{0.5}\text{FePO}_4$ composition during charge at 1C and C/5 rates. The diameter of the circle is 4 mm.

0 in charge and discharge at rates of 1C and 1D. The distribution of the Fe^{II} proportion is clearly heterogeneous with some parts of the electrode containing more LiFePO_4 than expected while other parts contained less LiFePO_4 . We also observed a clear influence of the hole in the experimental cell (dotted circle). This is probably due to the difference of applied pressure at the hole position where the electric contact with the current collector is less efficient. In this case, the heterogeneity is attributed to a limited electron transfer [2]. This important observation provides a reasonable explanation of the apparent delay observed in transmission XRD by several authors: the exposed zone for XRD shows a “delay” caused by smaller electrical contact (smaller applied pressure) at the centre of the electrode.

The strong influence of the regime on the heterogeneity of the electrode is shown in Fig. 6. For the same composition (charged at global composition $\text{Li}_{0.5}\text{FePO}_4$), transmission measurements show that the electrode is nicely homogeneous when charged at C/5. On the contrary, it is very much “delayed”, i.e. overlithiated locally and hence globally heterogeneous, when charged at 1C rate. Indeed, a higher current results in larger local polarization where the electron transfer is limited (in the centre of the electrode) and thus stronger delay.

These mapping experiments clearly demonstrate the heterogeneous behaviour of Li or electron diffusion within the electrode and much care has to be taken for analysing and interpreting XRD data wherein only a very small part of the electrode is screened.

6. Conclusion

Beyond the general hypothesis that heterogeneous behaviour of an electrode is possible, it is important to visualize and quantify this behaviour so as to determine the more important parameters inducing such heterogeneity. A possible heterogeneity in the thickness of the electrode is generally expected mainly due to lithium ion diffusion. To address this diffusion issue synchrotron XAS experiments appear as a unique tool to follow the redox process taking place in the electrode battery materials, with a powerful combination of time and spatially resolved experiments. We have clearly demonstrated that an important heterogeneity may also appear in all parts of the electrode, some parts of the electrode being delayed in the phase transformation, as compared to the global lithium content and some others being in advance.

We have demonstrated the influence of two parameters, the pressure and the cycling rate that control the speed of electron supply to the active material. This led us to hypothesize that the key parameter of the heterogeneous behaviour is the quality of grain connectivity to ionic and electronic percolating networks. In order to validate this hypothesis, other parameters including particle size, electrode composition, electrode processing are now being investigated.

7. Methods

Well crystallized and monodispersed (diameter of 150 nm) primary particles of LiFePO_4 were used. During carbon coating, these primary particles were agglomerated as “balls” with diameters close to 20 μm . Electrodes were prepared using a doctor blade technique on a mixture of active material, Ketjenblack 300 as the conductive additive (provided by AkzoNobel) and Kynar Flex, a block copolymer containing PVdF and HFP (provided by Arkema), with a respective mass ratio of 66.7:13.3:20, mixed in acetone. In these experiments, we have used the specially designed *in situ* electrochemical cell described in reference 12. The electrode of 1 cm^2 of surface and about 100 μm in thickness was assembled into the in-situ cell versus a lithium foil anode, a Whatman GF/D borosilicate glass–fibre sheet as separator and 1 M LiPF_6 electrolyte solution in 1:1 ethyl carbonate/dimethyl carbonate (LP30). A typical electrode weights between 7 and 8 mg, corresponding to about 5 mg of active material. Electrochemical cycling was monitored using a VMP system (Bio-Logic®) in galvanostatic mode, between 2.0 and 4.2 V. The current was 170 mA g^{-1} (1C, where C is the rate at which the full charge capacity is delivered in 1 h). Data were collected in transmission mode on the SAMBA and ODE beamlines and then normalized by using the Athena software [22]. On the LUCIA beamline, data were simultaneously collected in transmission and fluorescence modes. On the SAMBA beamline, measurements which included both XANES and EXAFS techniques, were performed on the Q-EXAFS monochromator Si(111) with an oscillation frequency of 1 Hz (meaning one spectrum collected in 500 ms, well adapted to high rates). The X-ray beam 400 $\mu\text{m} \times 3 \text{ mm}$ permitted checking of the heterogeneity of the electrode at a large scale. For smaller scale, we used the dispersive XAS set-up on the ODE beamline equipped with a bent monochromator (311) that captures all angles simultaneously, thus eliminating the stepwise scanning of the X-ray energy. The main assets of dispersive XAS are the focussing optics (spot size 25 $\mu\text{m} \times 50 \mu\text{m}$) and more specially the short acquisition time (about 10 XANES spectra recorded in 1 s for our experiments). μXAS experiments were conducted on the LUCIA beamline equipped with a Si(111) double crystal monochromator. The monochromatic beam of 7 \times 7 μm^2 size is incident on a sample that is carried on a scanning x – z stage. Data have been collected simultaneously in transmission and in fluorescence modes.

Acknowledgement

The authors acknowledge the support of the French Agence Nationale de la Recherche (ANR) under reference ANR-07-Stock-E-09-01. Jean Bernard Leriche (LRCS) is gratefully acknowledged for his significant help in designing the electrochemical cell. We thank also Emiliano Fonda (Synchrotron SOLEIL) for the development of the scripting dedicated to kinetic experiments on the SAMBA beamline, and Pierre Lagarde (Synchrotron SOLEIL) for his essential help in map acquisition.

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